



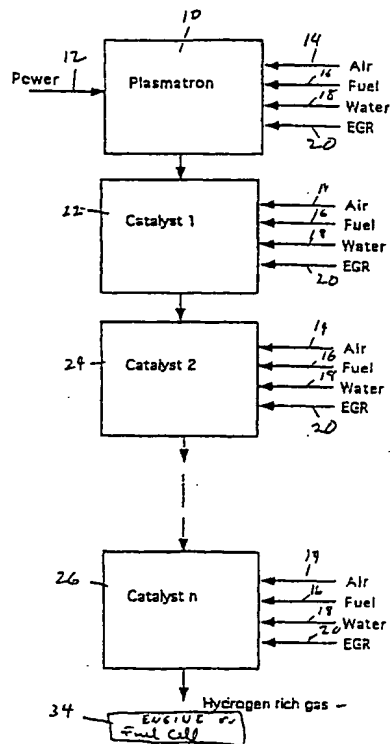
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : F02B 43/10, C01B 3/34, F02B 51/04		A1	(11) International Publication Number: WO 00/26518
			(43) International Publication Date: 11 May 2000 (11.05.00)
(21) International Application Number: PCT/US99/25179			(81) Designated States: CA, JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(22) International Filing Date: 27 October 1999 (27.10.99)			
(30) Priority Data: 09/182,537 29 October 1998 (29.10.98) US			
(71) Applicant: MASSACHUSETTS INSTITUTE OF TECHNOLOGY [US/US]; 77 Massachusetts Avenue, Cambridge, MA 02142 (US).			
(72) Inventors: BROMBERG, Leslie; 176 Wilshire Drive, Sharon, MA 02067 (US). RABINOVIC, Alexander; 404 Paradise Road #3L, Swampscott, MA 01907 (US). ALEXEEN, Nikolai; Pavla, Korchagina Street 15-00, Moscow, 129278 (RU). COHN, Daniel, R.; 26 Walnut Hill Road, Chestnut Hill, MA 02167 (US).			
(74) Agent: PASTERNAK, Sam; Choate, Hall & Stewart, Exchange Place, 53 State Street, Boston, MA 02109 (US).			

(54) Title: PLASMATRON-CATALYST SYSTEM

(57) Abstract

The system generates hydrogen-rich gas and comprises a plasmatron (10) and at least one catalyst (22) for receiving an output from the plasmatron (10) to produce hydrogen-rich gas. In a preferred embodiment, the plasmatron (10) receives as an input air (14), fuel (16) and water/steam (18) for use in the reforming process. The system increases the hydrogen yield and decreases the amount of carbon monoxide.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

PLASMATRON-CATALYST SYSTEM

This application is a continuation-in-part of U.S. Application Serial No. 08/589,119 filed January 19, 1996 for Rapid Response Plasma Fuel Converter Systems.

Background of the Invention

This invention relates to a plasmatron-catalyst system which can maximize hydrogen yield and decrease the amount of carbon monoxide.

The pending U.S. Application mentioned above, of which this application is a continuation-in-part, discloses and claims the use of a rapid response plasmatron for converting hydrocarbon fuels into hydrogen-rich gases. This process may be carried on-board vehicles.

Converting hydrocarbon fuels into hydrogen-rich gas (reforming) can be achieved with a plasmatron reactor. There are many advantages of using a plasmatron in the reforming process. Advantages include fast response (less than one second), adequate conversion into hydrogen-rich fuel, compactness (high hydrogen productivity), robustness (stable process), and the ability of the plasmatron to use many fuels, including hard-to-reform gasoline, diesel and biofuels.

For internal combustion applications, the hydrogen purity is not of great importance. High conversion efficiency into hydrogen is not necessary, since the low weight hydrocarbons that accompany the hydrogen produced by the plasmatron are also good fuels for use in internal combustion engines. More important is to minimize the energy consumed in the plasmatron during the reforming process.

U.S. Patent Nos. 5,425,332 and 5,437,250 disclose plasmatron-internal combustion engine systems and the teachings of these two patents are incorporated herein by reference. Plasmatrons of the type used in the present invention are described in detail in these two patents.

In the previous application mentioned above, partial oxidation is the preferred method of reforming. An advantage of partial oxidation is that it eliminates the need for storing additional liquids on-board vehicles. Also, in that application, a fraction of the fuel is reformed in order to allow the introduction into the cylinder of an engine hydrogen-rich gas to improve the combustion process. Since the intention in that application was not to reform all of the fuel, the issues of efficiency, although still relevant, do not drive the design of the plasmatron system.

The previous application discloses the use of plasma catalysis on-board vehicles. The process of converting the hydrocarbon into hydrogen rich gases by the use of plasma catalysis addresses mainly the energy requirement in the plasmatron in the reformation process. Plasma catalysis, as used for applications in internal combustion engines, can decrease the electrical energy requirement. The earlier patent application did not suggest the use of catalysts to maximize hydrogen yield nor to decrease the amount of CO (carbon monoxide) that is produced in the partial oxidation process (The hydrogen yield is defined as the ratio of the hydrogen in the reformat to the amount of hydrogen content in the fuel).

The earlier pending application did not extend plasma catalysis into the context of fuel cell vehicles and stationary fuel cells in which very high hydrogen yields and low energy consumption are required.

The requirements on a reformat for fuel cell applications are very different from those for use of hydrogen rich gas in internal combustion engines. As described above, for application to internal combustion engines, it is not necessary to have high yields, a very efficient process or very clean gas. As used herein, clean gas is defined to be gas with small concentrations of CO, since CO is a poison to some types of fuel cells that are presently being considered for both stationary and vehicular applications, of which the PEM fuel cell is the most advanced candidate. U.S. Patent No. 5,409,784 discloses plasmatron/fuel cell combinations and the teachings of this patent are incorporated herein by reference.

The pending patent application of which this application is a continuation-in-part also did not disclose the possible use of water/steam in the reforming process.

5

Summary of the Invention

10 In one aspect, the plasmatron-catalyst system of the invention for generating hydrogen rich gas includes a plasmatron and at least one catalyst for receiving an output from the plasmatron to produce hydrogen rich gas. In a preferred embodiment, the plasmatron receives as an input air, fuel and water/steam. The plasmatron may also receive exhaust gas from an engine or fuel cell. It is preferred that the at least one catalyst receive as an input air, fuel and water/steam. The catalyst may also receive exhaust gas from an engine or fuel cell.

15

In another embodiment, the at least one catalyst includes a heat exchanger in heat exchange relation with the catalyst to preheat the air, fuel and water/steam. One embodiment includes a plurality of catalyst sections wherein each catalyst section receives additional air, fuel or water/steam.

20

In another aspect, the plasmatron catalyst system further includes a fuel cell for receiving the hydrogen rich gas, the hydrogen rich gas having reduced CO content. The fuel cell may be in a vehicle or in a stationary setting.

25

In another embodiment, the plasmatron is followed by fuel injection system for a partial oxidation process, the fuel injection system followed by a catalyst for improved yields, the catalyst followed by water/steam injection and a water-shift reformer catalyst whereby hydrogen concentration is increased and CO concentration is decreased. In any of these embodiments, the catalyst may be a water-shifting catalyst. The catalyst may also be a partial oxidation catalyst or a steam reforming catalyst. In yet another embodiment, the catalysts are a combination of partial oxidation, steam reforming or water-shift catalyst with possible addition of water/steam in between adjacent catalytic regions.

30

In another embodiment, the steam reforming catalyst is followed by a water-shifting catalyst, with or without additional water/steam injection prior to the water-shifting catalyst.

5 The present system may be operated in a less efficient non-catalytic mode of operation during cold start followed thereafter by more efficient catalytic plasma reforming after the catalyst reaches operating temperature. The water/steam may be obtained from oxidation of hydrogen in a fuel cell or by combustion in an engine such as a diesel engine. The water-steam may also be obtained from the exhaust of a diesel
10 engine.

 In yet another aspect, the hydrogen rich gas is delivered to a catalytic converter of an internal combustion engine wherein the enthalpy of the hydrogen-rich gas preheats and/or activates the catalyst in the catalytic converter. The hydrogen-
15 rich gas produced by the system of the invention may also be used for reducing processes in metallurgy and chemistry. The hydrogen-rich gases may also be used for hydrogenation as in food processing and fuel upgrading.

 In yet another embodiment, the CO content of the reformat is decreased by
20 the use of a non-thermal, catalytic reaction to selectively oxidize the CO to CO₂.

Brief Description of the Drawing

 Fig 1. is a block diagram of an embodiment of the invention illustrating
25 multiple catalyst sections.

 Fig 2. is a block diagram of an embodiment of the invention including a heat exchanger.

 Fig 3. is a block diagram of an yet another embodiment of the invention.

 Fig 4. is a block diagram of an embodiment of the invention including a
30 catalytic converter.

 Fig 5. is a block diagram of an embodiment of the invention including a non-thermal plasma catalyst.

Description of the Preferred Embodiment

Water/steam can be used to achieve several objectives in the reforming process. These objectives include use in a water-shift reaction, downstream from the plasmatron and reactor, in order to reduce the CO concentration and increase the hydrogen concentration. Water/steam can also be used to perform steam reforming in which the water/steam reacts with the hydrocarbon fuel to produce hydrogen and CO. Water/steam can also be used in an autothermal reaction in which both air and water/steam are used in order to insure that the exothermicity of the partial oxidation process is balanced by the endothermicity of the steam reforming reaction. In this case, the reforming reaction is energy neutral. The use of water/steam, oxygen and fuel in a plasmatron reactor forms a continuum of possibilities. In the case of partial oxidation, the maximum hydrogen yield is 100%, while when water/steam is added the hydrogen yield can be larger than 100% by virtue of the release of hydrogen from the water/steam.

It will be appreciated by those skilled in the art that exhaust gases, either from a fuel cell or an internal combustion engine may be used as an input to the plasmatron for reforming. In this case, the reformed gas composition is nitrogen, CO, CO₂, and water.

It has been demonstrated experimentally by the inventors herein, that by using catalysts downstream from the plasmatron, the electrical energy consumption in the plasmatron is reduced substantially (by a factor of 9) with increased hydrogen yields (approaching 100%) and with relatively small CO concentrations (at the present time, about 1-2%, but possibly smaller in the future with improved reactor design).

The need to preheat the catalyst slows down the response of a system operating in plasma catalysis mode. Fast response is needed, especially for on-board applications, for the fast generation of hydrogen during initial operation of a vehicle after a prolonged shut down. In order to allow for rapid response, the mode of operation of the plasmatron is varied. During cold starts, the plasmatron operates

with larger electrical input, resulting in gases with high enthalpy, that allows for high yields without the need of the catalyst, but at the expense of increased energy consumption. In other words, during cold start the system operates in a non-catalytic mode. Once the catalysts are warmed up, the plasmatron energy input is decreased to the steady state level allowed by the more efficient plasma catalyst.

The hydrogen rich gas from the plasmatron may also be introduced into the catalytic convertor that is used to control emissions from an internal combustion engine. The hydrogen and radicals produced by the plasmatron interact with the catalyst, making it more active. In addition, combustion of the hydrogen rich gas on the catalytic surface increases the temperature of the catalyst, and can be used for quick turn-on of catalyst during cold start-up. The long-lived radicals produced by the plasmatron also enhance the catalytic performance of the convertor.

The hydrogen productivity in plasma-catalytic mode, with water/steam injection, can be very high, generating about 10 cubic meters of hydrogen per liter of reactor.

With reference now to Fig. 1, a plasmatron 10 is supplied with electrical power 12. It is contemplated that this plasmatron will also receive as input air 14, fuel 16, water 18 and optionally exhaust gas 20. In this embodiment, the output of the plasmatron 10 passes into a first catalyst section 22 and from there into a second catalyst section 24. Any number of additional catalyst sections may be added up to catalyst n illustrated at 26 in Fig. 1. The catalyst used in the catalyst sections may be a water-shifting catalyst, a partial oxidation catalyst or a steam reforming catalyst.

With reference to Fig. 2 a, a heat exchanger 28 is provided in heat exchange relation with catalyst n . The heat exchanger 28 will preheat the air, fuel and water before it enters the plasmatron 10. A similar arrangement is shown in Fig. 3 in which the heat exchanger 28 serves to preheat fuel, air and water before it enters the catalyst 22.

A very important aspect of the present invention is illustrated in Fig. 4. In this embodiment, the output of the plasma and the multiple catalyst stages is directed to a catalytic converter 30 such as conventionally used with internal combustion engines. In this case, the hydrogen-rich gas and radicals produced by the plasmatron interact with the catalyst making it more active. In addition, air and fuel may be injected into the catalytic converter 30 so that combustion of the hydrogen-rich gas on the catalytic surface increases the temperature of the catalyst and can be used for quick turn-on of the catalyst during cold start up.

Finally, with reference to Fig. 5, the output of the plasmatron-catalyst system is introduced into a non-thermal plasma catalyst of 32 which produces a hydrogen-rich gas with a low CO content.

With reference again to Fig. 1, those skilled in the art will recognize that hydrogen rich gas from the last catalyst stage may be delivered to an engine or fuel cell 34.

It is thus seen that the present invention results in a rapid response plasmatron/catalyst system which can maximize the hydrogen yield and decrease the amount of carbon monoxide by using water/steam in the reforming process.

It is recognized that modifications and variations of the present invention will occur to those skilled in the art and it is intended that all such modifications and variations be included within the scope of the pended claims.

What is claimed is:

- 1 1. Plasmatron-catalyst system for generating hydrogen-rich gas comprising:
2 a plasmatron; and
3 at least one catalyst for receiving an output from the plasmatron to produce
4 hydrogen-rich gas.
- 5 2. The system of claim 1 wherein the plasmatron receives as an input air, fuel
6 and water/steam.
- 7 3. The system of claim 2 further including the plasmatron receiving exhaust gas
8 from an engine or fuel cell.
- 9 4. The system of claim 1 wherein the at least one catalyst receives as an input air,
10 fuel and water/steam.
- 11 5. The system of claim 4 wherein the at least one catalyst receives exhaust gas
12 from an engine or fuel cell.
- 13 6. The system of claim 2 wherein the at least one catalyst includes a heat
14 exchanger in heat exchange relation with the catalyst to preheat the air, fuel and
15 water/steam.
- 16 7. The system of claim 1 including a plurality of catalyst sections, wherein each
17 catalyst section receives additional air/fuel or water/steam.
- 18 8. The system of claim 1 further including a fuel cell for receiving the hydrogen-
19 rich gas, the hydrogen-rich gas having reduced CO content.
- 20 9. The system of claim 8 wherein the plasmatron-catalyst system is in a vehicle.
- 21 10. The system of claim 8 wherein the plasmatron-catalytic system is stationary.
- 22 11. The system of claim 1 wherein the plasmatron is followed by a fuel injection
23 system for a partial oxidation process, the fuel injection system followed by a catalyst
24 for improved yields, the catalyst followed by water/steam injection and a water-shift
25 reformer catalyst whereby hydrogen concentration is increased and CO concentration
26 is decreased.
- 27 12. The system of any of claims 1-11 wherein the catalyst is a water-shifting
28 catalyst.
- 29 13. The system of claim 12 wherein the catalyst is a partial oxidation catalyst.
- 30 14. The system of claim 12 wherein the catalyst is a steam reforming catalyst.

- 1 15. The system of claim 11 wherein the catalysts are a combination of partial
2 oxidation, steam reforming or water-shift catalyst, with possible addition of
3 water/steam between adjacent catalytic regions.
- 4 16. The system of claim 15 wherein the steam reforming catalyst is followed by
5 water-shifting catalyst with or without additional water/steam injection prior to the
6 water-shifting catalyst.
- 7 17. The system of claim 2 wherein the water/steam is obtained from oxidizing
8 hydrogen in a fuel cell or by combustion in an engine.
- 9 18. The system of claim 17 wherein an engine is a diesel engine.
- 10 19. The system of claim 2 wherein the water/steam is obtained from the exhaust
11 from a diesel engine.
- 12 20. The system of claim 1 or claim 2 wherein the hydrogen-rich gas is delivered to
13 a catalytic converter of an internal combustion engine wherein enthalpy of the
14 hydrogen-rich gas preheats and/or activates the catalyst
- 15 21. The system of claim 1 or claim 2 wherein the hydrogen-rich gas is used for
16 reduction processes in metallurgy and chemistry.
- 17 22. The system of claim 1 or claim 2 wherein the hydrogen-rich gas is used for
18 hydrogenation as in food processing and fuel upgrading.
- 19 23. The system of claim 1 or claim 2 further including a non-thermal catalytic
20 reaction element to selectively oxidize CO to CO₂.
- 21

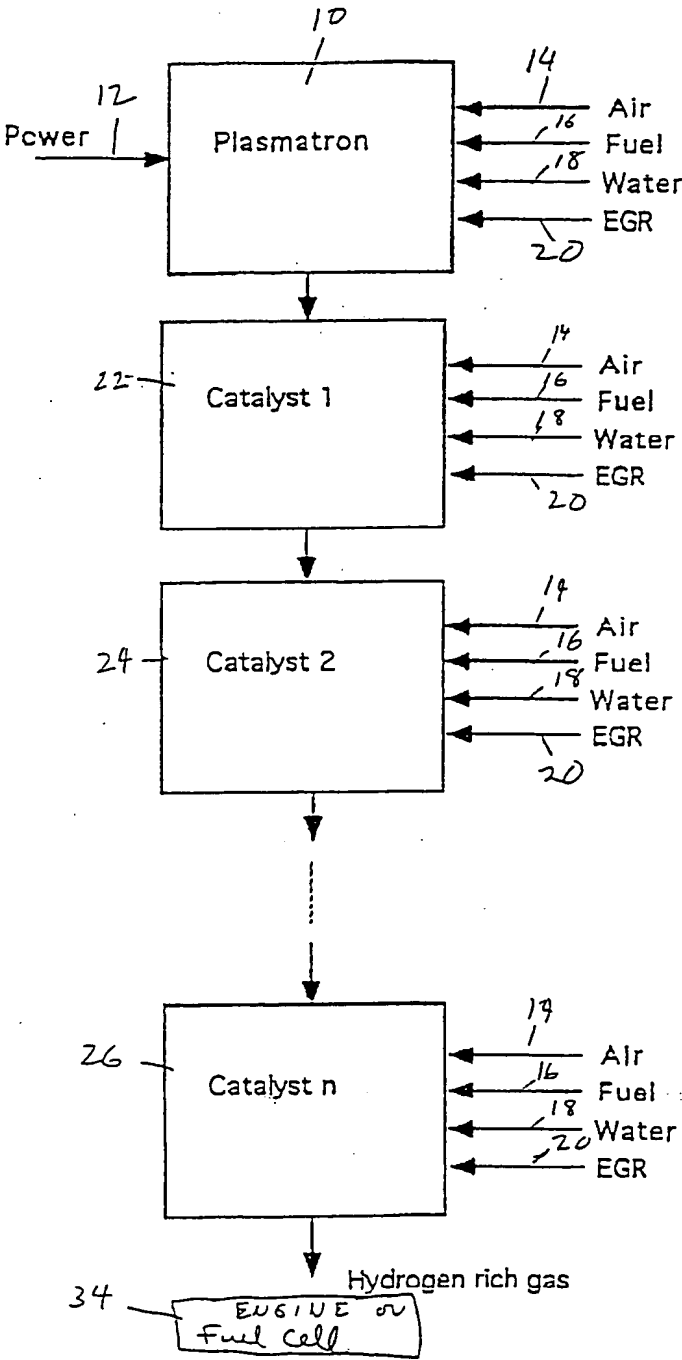


Figure 1

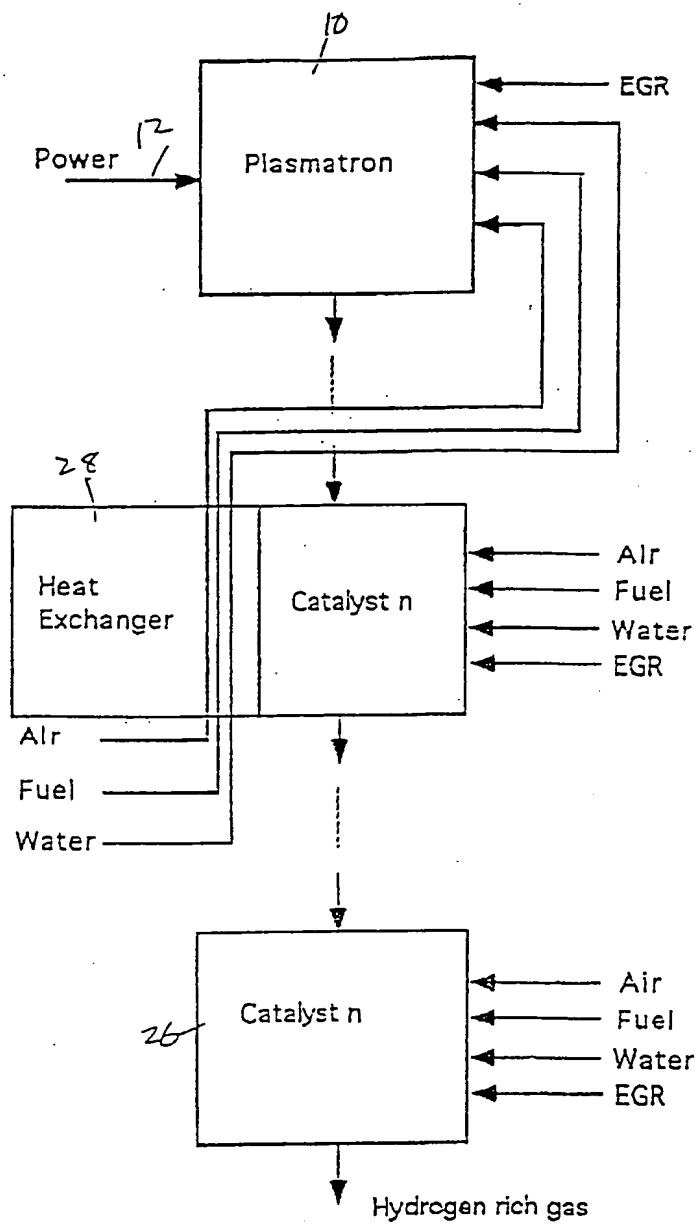


Figure 2

3/5

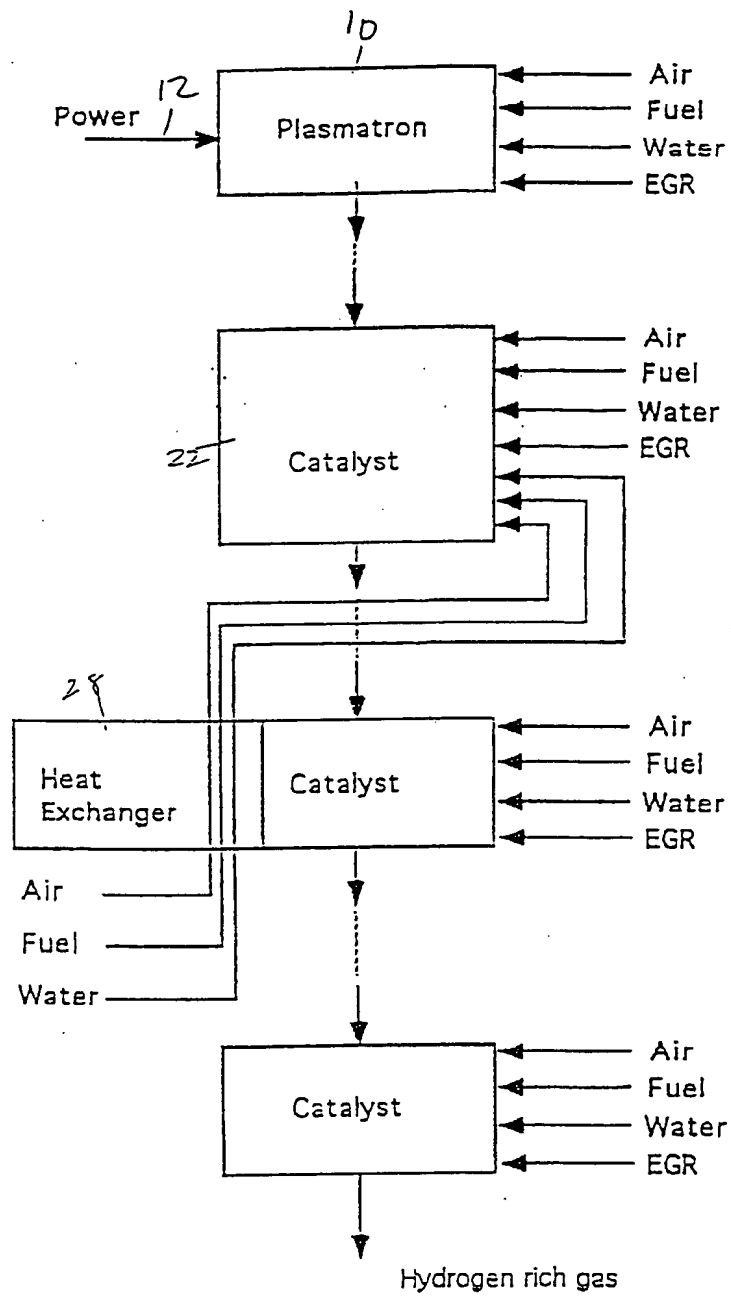


Figure 3

4/5

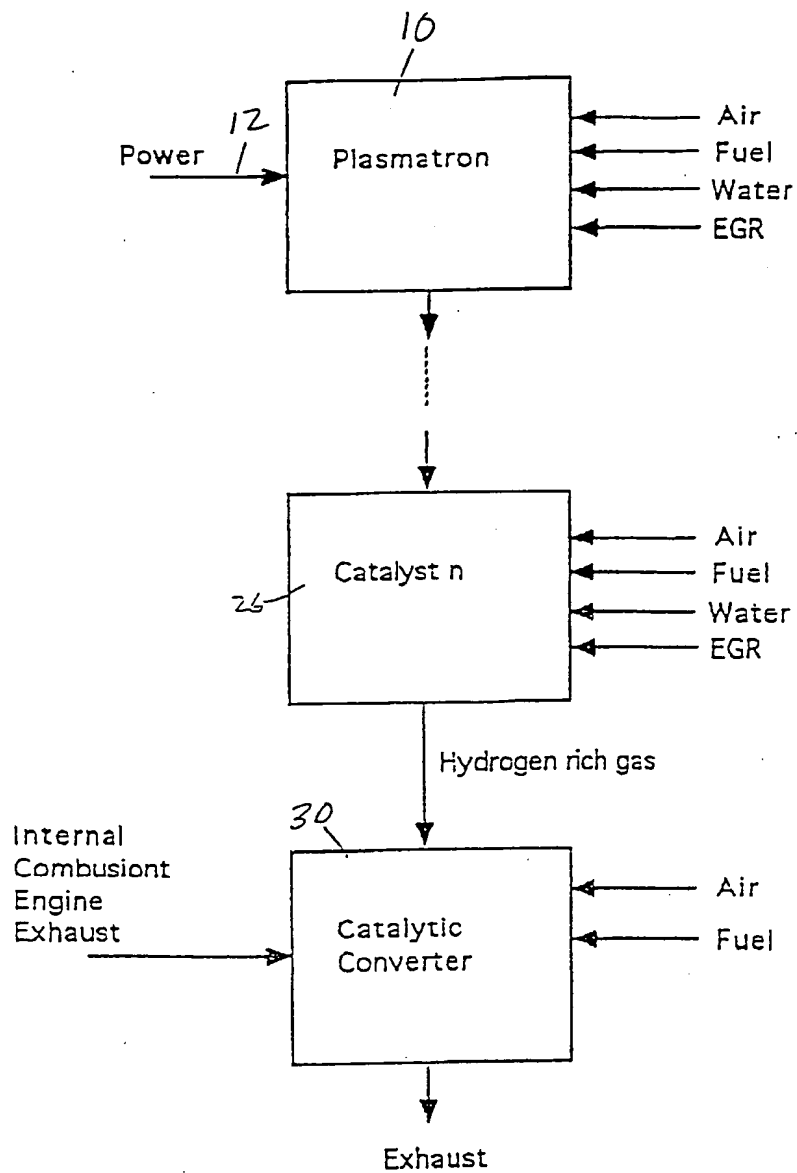


Figure 4

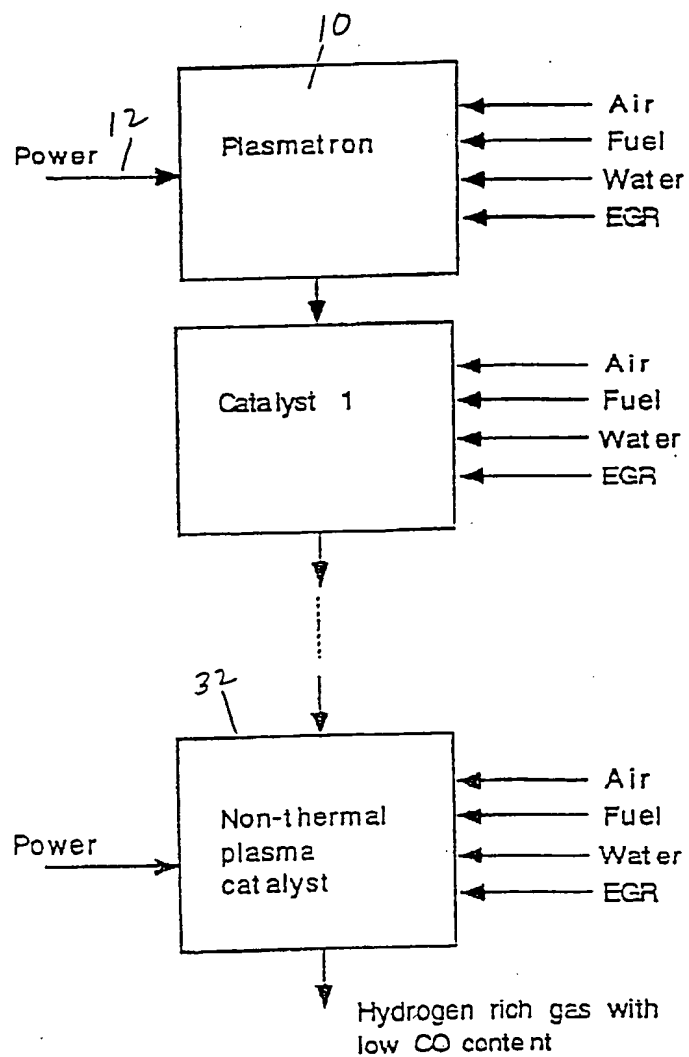


Figure 5

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/25179

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 F02B43/10 C01B3/34 F02B51/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 F02B C01B H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	US 5 887 554 A (COHN DANIEL R ET AL) 30 March 1999 (1999-03-30) column 9, line 50 -column 10, line 18; figure 9 ---	1,6,9, 10,20
X	GB 355 210 A (RUHRCHEMIE AG) 1931 the whole document ---	1
A	EP 0 807 154 A (BATTELLE MEMORIAL INSTITUTE ;TITUS CHARLES H (US); COHN DANIEL R () 19 November 1997 (1997-11-19) ---	
A	US 5 437 250 A (COHN DANIEL R ET AL) 1 August 1995 (1995-08-01) cited in the application --- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

28 January 2000

Date of mailing of the international search report

03/02/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

von Arx, H

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/25179

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 425 332 A (COHN DANIEL R ET AL) 20 June 1995 (1995-06-20) cited in the application ----	
A	US 5 409 784 A (COHN DANIEL R ET AL) 25 April 1995 (1995-04-25) cited in the application ----	
P, A	US 5 852 927 A (COHN DANIEL R ET AL) 29 December 1998 (1998-12-29) -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/25179

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5887554 A	30-03-1999	NONE	
GB 355210 A		NONE	
EP 0807154 A	19-11-1997	US 5666891 A US 5798497 A AU 711952 B AU 6347096 A JP 10513255 T NZ 305522 A CA 2212152 A WO 9624441 A US 5811752 A US 5756957 A US 5847353 A US 5908564 A	16-09-1997 25-08-1998 28-10-1999 27-08-1996 15-12-1998 28-01-1999 15-08-1996 15-08-1998 22-09-1998 26-05-1998 08-12-1998 01-06-1999
US 5437250 A	01-08-1995	US 5425332 A AT 166135 T AU 7671694 A DE 69410276 D DE 69410276 T EP 0715683 A ES 2119224 T WO 9506194 A	20-06-1995 15-05-1998 21-03-1995 18-06-1998 17-12-1998 12-06-1996 01-10-1998 02-03-1995
US 5425332 A	20-06-1995	AT 166135 T AU 7671694 A DE 69410276 D DE 69410276 T EP 0715683 A ES 2119224 T WO 9506194 A US 5437250 A	15-05-1998 21-03-1995 18-06-1998 17-12-1998 12-06-1996 01-10-1998 02-03-1995 01-08-1995
US 5409784 A	25-04-1995	WO 9517021 A	22-06-1995
US 5852927 A	29-12-1998	NONE	